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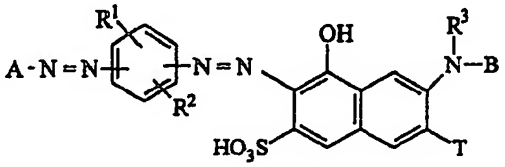
(54) Disazo compound

(57) Disazo dyes have the Formula (1):



Formula (1)

wherein:

A	is optionally substituted phenyl or naphthyl;
R^1	is NR^4R^5;
R^2	is H, halo, -COOH, $-SO_2OH$, optionally substituted alkyl, alkoxy or alkylthio;
R^3 and R^4	are each independently is H or optionally substituted alkyl;
R^5	is optionally substituted acyl;
T	is H or sulpho; and
B	is H, optionally substituted alkyl or phenyl.

provided that the compound does not contain a piperazinyl group, and the compound may be in the form of a salt.

The compound is suitable for use as a black colourant in ink jet printing inks especially for printing on plain paper.

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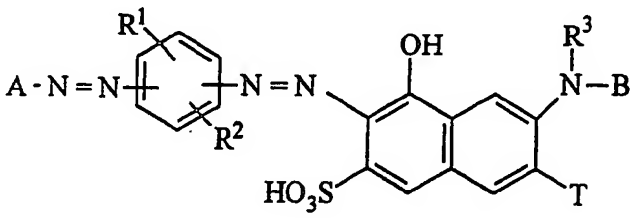
DISAZO COMPOUND

This invention relates to a coloured disazo compound and aqueous solutions thereof suitable for use in the coloration of substrates, especially sheet materials such as paper, and especially by a printing process such as ink jet printing.

According to a first aspect of the present invention there is provided a compound of the Formula (1) and salts thereof:



Formula (1)

wherein:

A is optionally substituted phenyl or naphthyl;

R^1 is NR^4R^5;

R^2 is H, halo, -COOH, $-SO_2OH$, optionally substituted alkyl, optionally substituted alkoxy, or optionally substituted alkylthio;

R^3 & R^4 are each independently is H or optionally substituted alkyl;

R^5 is optionally substituted acyl;

T is H or sulpho; and

B is H, optionally substituted alkyl or optionally substituted phenyl.

provided that the compound does not contain a piperazinyl group.

It is preferred that the compound of Formula (1) or (2) has at least as many carboxy (-COOH) groups as sulpho ($-SO_2OH$) groups, more preferably not more than 2 sulpho groups and especially only a single sulpho group. It is preferred that the compound of Formula (1) or (2) has from 1 to 5, more preferably from 1 to 3, and especially 2 or 3 carboxy groups.

When A is substituted it preferably carries from one to three, especially one or two, substituents selected from:

- carboxy; sulpho; -OH; -CN; $-NO_2$; $-PO(OH)_2$; $-B(OH)_2$;
- halo, preferably -Cl;
- alkyl, preferably C_{1-4}-alkyl and especially methyl;
- alkoxy, preferably C_{1-4}-alkoxy and especially methoxy;
- $-COOR^3$, wherein R^3 is as hereinbefore defined other than H;

- $-SO_2R^6$ or $-COR^6$, wherein R^6 is optionally substituted C_{1-4}-alkyl or optionally substituted aryl;
- optionally substituted amino, preferably $-NQ^1Q^2$ wherein Q^1 and Q^2 are each independently H or optionally substituted alkyl or aryl, or Q^1 and Q^2, taken together with the N atom to which they are attached, form an optionally substituted ring, especially morpholine or piperidine ring; and
- acylamino, especially alkyl- or aryl-carbonylamino or alkyl- or aryl-sulphonylamino, more especially C_{1-4}-alkyl-CONH- or C_{1-4}-alkyl-SO_2NH-.

It is, however, preferred that A does not contain a heterocyclic group.

It is especially preferred that A is carboxyphenyl or carboxynaphthyl, especially 3- or 4-carboxyphenyl group or carboxyphenyl having one or two further substituents, especially one, selected from carboxy, sulpho, methyl, methoxy and chloro. Examples of optionally substituted phenyl and naphthyl groups represented by A are 4-carboxy-phenyl, 3-carboxy-phenyl, 3,5-dicarboxy-phenyl, 3,4-dicarboxyphenyl, 2-methyl-5-carboxyphenyl, 2-methoxy-5-carboxyphenyl, 2-chloro-5-carboxy-phenyl, 2-sulpho-5-carboxyphenyl, 3- or 4-amino-5-carboxyphenyl, 4-acetylamino-3-carboxyphenyl, 4-carboxynaphth-1-yl, 5-carboxynaphth-1-yl, 6-carboxynaphth-1-yl, 7-carboxynaphth-1-yl, 6-carboxynaphth-2-yl and 1-sulpho-6-carboxynaphth-2-yl.

When R^6, Q^1 or Q^2 is optionally substituted alkyl it is preferably C_{1-4}-alkyl, such as methyl, ethyl, propyl or butyl. When R^6, Q^1 or Q^2 is optionally substituted aryl it is preferably phenyl.

R^2 is preferably C_{1-4}-alkyl, especially methyl or ethyl; C_{1-4}-alkoxy, especially methoxy or ethoxy, C_{1-4}-alkylthio, especially methylthio; Cl; H; COOH; or SO_2OH. R^3 is preferably H or C_{1-4}-alkyl, more preferably H, methyl or ethyl.

R^4 is preferably H or C_{1-4}-alkyl, and more especially H.

The acyl group, R^5, is preferably NH_2CO-, R^6CO- or R^6SO_2-, wherein R^6 is as hereinbefore defined, i.e. optionally substituted C_{1-4}-alkyl or optionally substituted aryl, especially phenyl.

Where Q^1, Q^2, R^2, R^3, R^4, R^5 or R^6 is substituted alkyl or substituted alkoxy, or Q^1 and Q^2 form a ring, the substituent(s) is preferably selected from -COOH, $-SO_2OH$, OH, NH_2, C_{1-4}-alkoxy and halo, especially chloro. Where R^6, Q^1 or Q^2 is substituted aryl it is preferably phenyl and the substituent(s) is preferably in the 2-, 4-, 2,4-, 3,4- and 3,5-position(s) and selected from -COOH; $-SO_2OH$; OH; NH_2, CN; NO_2; C_{1-4}-alkyl; C_{1-4}-alkoxy; and halo, especially chloro.

The optionally substituted phenyl group, B, may carry one or more substituents selected from the same group of optional substituents as on A, especially sulpho; carboxy; C_{1-4}-alkyl; C_{1-4}-alkoxy; and chloro. It is preferred that B is unsubstituted phenyl or phenyl substituted by

one or two carboxy groups and optionally by one or more other substituents selected from those listed above as optional substituents.

The optionally substituted alkyl group represented by B is preferably C_{1-4}-alkyl which may be unsubstituted or may carry one or more substituents selected from $-SO_2OH$, OH, amino, especially NH_2, morpholino, C_{1-4}-alkoxy and halo, and more especially -COOH. It is preferred that B is H or unsubstituted phenyl or C_{1-4}-alkyl or phenyl or C_{1-4}-alkyl substituted by one or two carboxy groups.

Examples of preferred optionally substituted phenyl groups represented by B are phenyl, 4-carboxy-phenyl, 3-carboxyphenyl, 3,5-dicarboxyphenyl, 3,4-dicarboxyphenyl, 2-methyl-5-carboxyphenyl and 2-sulpho-5-carboxyphenyl. Examples of preferred alkyl groups represented by B are H, methyl, ethyl, propyl, butyl, carboxymethyl and 2-carboxy-ethyl.

Where B is free of carboxy groups it is preferred that A carries at least one, and more preferably, two carboxy groups and where A is free of carboxy groups it is preferred that B carries at least one, and more preferably, two carboxy groups.

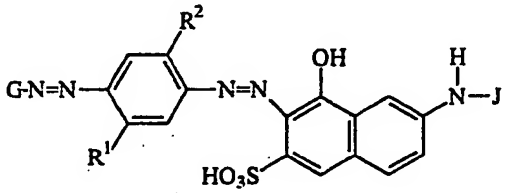
It is preferred that T is H.

A preferred compound of Formula (1) is where A is optionally substituted carboxyphenyl wherein any further substituent is selected from -COOH, $-SO_2OH$, methyl, methoxy, chloro, NH_2 and hydroxy, especially 3- or 4-carboxyphenyl or 3,4- or 3,5-dicarboxyphenyl; R^2 is H, methoxy or methyl; R^4 is H or C_{1-4}-alkyl; R^5 is $-CO-C_{1-4}$-alkyl, especially acetyl or propionyl, or -CO-aryl, especially benzoyl; T and R^3 are both H; and B is phenyl optionally having one or two carboxy substituents, especially phenyl, 3- or 4-carboxyphenyl or 3,4- or 3,5-dicarboxyphenyl. An especially preferred compound is where A is 3- or 4-carboxyphenyl or 3,4- or 3,5-dicarboxyphenyl; B is phenyl or selected from the groups represented by A; R^2 is H, methyl or methoxy; R^5 is acetyl or propionyl; and R^3, R^4 and T are H.

Another preferred compound of Formula (1) is where A is optionally substituted carboxyphenyl wherein any further substituent is selected from -COOH, $-SO_2OH$, methyl, methoxy, chloro and hydroxy, especially 3- or 4-carboxyphenyl or 3,4- or 3,5-dicarboxyphenyl; R^2 is H, methoxy or methyl; R^4 is H or C_{1-4}-alkyl; R^5 is $-CO-C_{1-4}$-alkyl, especially acetyl or propionyl, or -CO-aryl, especially benzoyl; T and R^3 are both H; and B is H or C_{1-4}-alkyl optionally having one or two carboxy substituents, such as methyl, ethyl, carboxymethyl or 2-carboxy-ethyl. An especially preferred compound is where A is 3- or 4-carboxy-phenyl or 3,4- or 3,5-dicarboxyphenyl; B is H, methyl or ethyl; R^2 is H, methyl or methoxy; R^5 acetyl or propionyl; and R^3, R^4 and T are H.

In the compound of Formula (1) it is preferred that the two azo groups are in para (1,4) relationship across the central phenylene group and that R^1 and R^2 are also in para (1,4) relationship across the central phenylene group. It is also preferred that R^1 is ortho to the azo group linking A to the central phenylene group and that R^2 is ortho to the azo group linking the Gamma acid moiety to the central phenylene group.

In the compound of Formula (1) it is preferred that all carboxy groups are in positions which are not adjacent to groups with which they can form intramolecular hydrogen bonds, such as $-NH_2$, -NH- and -OH groups. Accordingly a preferred compound according to the invention is of Formula (2) or a salt thereof:



Formula (2)

wherein:

G is 3-carboxyphenyl, 4-carboxyphenyl, 3,4-dicarboxyphenyl, 3,5-dicarboxyphenyl, or 2-methyl-5-carboxyphenyl;

J is H, methyl, ethyl, carboxymethyl, 2-carboxyethyl, phenyl, 3-carboxyphenyl, 4-carboxyphenyl, 3,4-dicarboxy-phenyl or 3,5-dicarboxyphenyl; and

R^1 and R^2 are as hereinbefore defined.

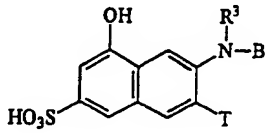
In the compound of Formula (2) it is preferred that R^1 is $-NHCO-C_{1-4}$-alkyl, especially acetylamino; and R^2 is H, C_{1-4}-alkyl, especially methyl or C_{1-4}-alkoxy, especially methoxy. It is especially preferred that R^1 is acetylamino and R^2 is methoxy.

The compounds of Formula (1) may be in the free acid form, as shown, but are preferably in the form of their salts with a cation such as an alkali metal, ammonium or optionally substituted C_{1-4}-alkyl-ammonium cation or a mixture of such cations. The preferred C_{1-4}-alkyl-ammonium cations consist of a nitrogen atom having four substituents selected from H, C_{1-4}-alkyl and hydroxy-C_{1-4}-alkyl, for example mono-, di-, tri- and tetra-(C_{1-4}-alkyl)-ammonium and mono-, di-, tri- and tetra-(hydroxy-C_{1-4}-alkyl)ammonium. It is, however, especially preferred that the cation is ammonium (i.e. NH_4^+), methylammonium, dimethylammonium or triethylammonium or that the dye of Formula (1) is in the form of a

mixed salt with alkali metal, especially lithium, sodium, and ammonium cations.

Examples of optionally substituted C_{1-4}-alkylammonium cations include methylammonium, ethylammonium, dimethylammonium, diethylammonium, trimethylammonium, triethylammonium, tri-(2-hydroxyethyl)-ammonium and tetramethylammonium.

The present compounds can be prepared by diazotising an amine of formula A-NH_2, preferably below 5°C using a nitrite and mineral acid, coupling with a substituted aniline carrying R^1 and R^2 to give a monoazo compound, diazotising the resultant monoazo compound and coupling with a compound of Formula (3):



Formula (3)

Compounds of Formula (3) in which B and R^3 are other than H, may be prepared using the Bucherer reaction in which 1-hydroxy-3-sulpho-7-hydroxy (or 7-amino)-naphthalene or 1-hydroxy-3,6-disulpho-7-hydroxy (or 7-amino)-naphthalene is reacted with an amine, R^3NHB, in the presence of an alkali metal or ammonium sulphite and bisulphite (e.g. Na_2SO_3 and $NaHSO_3$) with heating, preferably from 60-100°C and especially 70-90°C. In these processes A, R^1, R^2, R^3, T and B are as hereinbefore defined.

The present invention relates not only to a compound of Formula (1), but also to a composition comprising two or more compounds of Formula (1). An example of such a composition is a mixture containing two compounds of Formula (1) in which T, R^1, R^2 and R^3 are identical in both compounds but the identities of A and/or B differ. It is preferred that such a composition contains two compounds of Formula (1) in a weight ratio of 99:1 to 1:99, more preferably 90:10 to 10:90, especially 80:20 to 20:80, more especially 60:40 to 40:60.

The compound or composition of the present invention can be converted into its ammonium or optionally substituted lower alkylammonium salt by dissolving the compound in the form of a salt with an alkali metal, acidifying with a mineral acid, e.g. HCl, adjusting the solution to pH 9-9.5 with ammonia or an optionally substituted lower alkylamine and removing alkali metal and chloride ions by dialysis.

It will be understood that the present invention covers all tautomeric forms of a compound of Formula (1), e.g. the tautomeric

equivalent of Formula (1) in which the hydroxy group on the Gamma acid moiety is in the keto form.

A compound or composition of the present invention, particularly in the form of its ammonium or optionally substituted lower alkylammonium salt, is a useful colorant for an ink. It exhibits high solubility in water and aqueous media and good water fastness and gives a print with a strong black shade on plain paper. Compounds wherein R^1 is acetylamino and R^2 is H, alkyl, especially methyl or alkoxy, especially methoxy, perform particularly well. The compound and composition are versatile, exhibiting high water fastness on alkaline, neutral and acid papers, good solubility in aqueous ink media, minimal bronzing and give strong black images.

A suitable ink comprises a compound or a composition according to the present invention and a liquid medium, preferably an aqueous medium. It is preferred that the compound or composition is completely dissolved in the liquid medium to form a solution.

The ink preferably contains from 0.5% to 20%, more preferably from 0.5% to 15%, and especially from 1% to 3%, by weight of the compound or composition, based on the total weight of the ink. Although many inks contain less than 5% by weight of colorant, it is desirable that the compound or composition has a water solubility of around 10% or more to allow the preparation of concentrates from which more dilute inks can be prepared and to minimise the chance of precipitation of colorant if evaporation of solvent occurs during use of the ink.

The liquid medium is preferably water or a mixture comprising water and a water-soluble organic solvent, preferably in a weight ratio from 99:1 to 1:99, more preferably from 95:1 to 50:50 and especially from 90:10 to 60:40.

The water-soluble organic solvent is preferably a C_{1-4}-alkanol such as methanol, ethanol, n-propanol, i-propanol, n-butanol, s-butanol, t-butanol or i-butanol; an amide such as dimethylformamide or dimethyl-acetamide; a ketone or ketone alcohol such as acetone or diacetone alcohol; an ether such as tetrahydrofuran or dioxane; an oligo- or poly-(alkylene glycol) such as diethylene glycol, triethylene glycol, polyethylene glycol or polypropylene glycol; an alkylene glycol or thioglycol containing a C_2-C_6-alkylene group such as ethylene glycol, propylene glycol, butylene glycol, pentylene glycol or hexylene glycol and thiodiglycol; a polyol such as glycerol or 1,2,6-hexanetriol; a lower alkyl ether of a polyhydric alcohol such as 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxy-ethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]ethanol; a hetero-cyclic ketone, such as 2-pyrrolidone and N-methyl-2-pyrrolidone; or a

mixture containing two or more of the aforementioned water-soluble organic solvents, for example thiodiglycol and a second glycol or diethylene glycol and 2-pyrrolidone.

Preferred water-soluble organic solvents are selected from 2-pyrrolidone, N-methylpyrrolidone, alkylene glycol and oligo-(alkylene glycol)s such as ethylene glycol, diethylene glycol, triethylene glycol and lower alkyl ethers of polyhydric alcohols such as or 2-methoxy-2-ethoxy-2-ethoxyethanol; and polyethylene glycols with a molecular weight of up to 500. A preferred specific solvent mixture is a binary or ternary mixture of water and/or diethylene glycol and/or, 2-pyrrolidone or N-methylpyrrolidone in a weight ratios 75-95:25-5 and 60-80:0-20:0-20 respectively.

Examples of suitable ink media are given in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

A further aspect of the present invention provides a process for printing a substrate with an ink using an ink jet printer, characterised in that the ink contains at least one compound according to the first aspect of the present invention.

A suitable process for the application of an ink as herein-before defined comprises forming the ink into small droplets by ejection from a reservoir through a small orifice so that the droplets of ink are directed at a substrate. This process is commonly referred to as ink jet printing, and the ink jet printing processes for the present inks are preferably piezoelectric ink jet printing and, more especially, thermal ink jet printing. In thermal ink jet printing, programmed pulses of heat are applied to the ink in the reservoir by means of a resistor adjacent to the orifice, during relative movement between the substrate and the reservoir.

A preferred substrate is an overhead projector slide or a cellulosic substrate, especially cotton or paper, including plain and treated papers, which may have an acid, alkaline or neutral character.

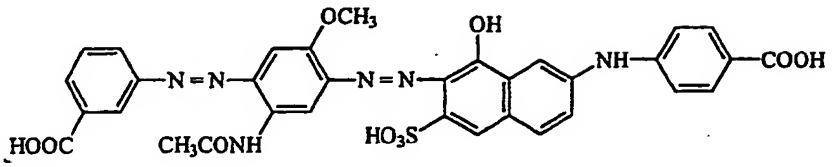
The preferred ink used in the process is as hereinbefore described.

According to a still further aspect of the present invention there is provided a paper or an overhead projector slide carrying a printed image comprising a compound of Formula (1) as defined herein.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise indicated.

Example 1

Preparation of the Compound of Formula (A)



(A)

Stage 1

To a stirred suspension of 3-aminobenzoic acid (27.4g) in ice/water (500ml), 36°Tw Hcl (50ml) was added, followed by a solution of $NaNO_2$ (15.2g) in water (100ml), maintaining the temperature at 0-10°C by the addition of small quantities of ice as necessary. When the addition was complete the resultant diazo solution was stirred at 0-10°C for 1 hour and residual HNO_2 destroyed by the addition of sulphamic acid.

3-Amino-4-methoxyacetanilide (40g) was dissolved in methylated spirits 740P (500ml) and added to the above diazo solution at 0-10°C and the mixture was stirred for 18 hours, allowing the temperature to rise to 20°C. The precipitated product was filtered off and the filter cake washed with water (2000ml) and dried at 60°C.

Stage 2

The product of Stage 1 (19.7g) was dissolved in water (500ml) at room temperature (by the addition of NaOH liquor to raise the pH to 10-11) and a solution of $NaNO_2$ (4.5g) in water (50ml) then added. This solution was added to a mixture of HCl (36°Tw, 30ml) and ice-water (100ml) over 10 minutes, maintaining the temperature at 0-10°C. After 2 hours at 0-10°C, excess HNO_2 was destroyed by addition of sulphamic acid, to give a diazo solution.

p-Carboxyphenyl-Gamma acid (25g) was dissolved in water (400ml) by adding NaOH liquor to pH 9.0 and the solution was cooled to 0-10°C. The diazo solution was added slowly over 10 minutes to the solution of p-carboxyphenyl-Gamma acid, maintaining the pH at 8-9 by addition of 2N NaOH solution. The mixture was then heated to 50-60°C and salted with 7% NaCl. The precipitated product of Formula (A) (mainly Na salt) was filtered and washed with 10% NaCl solution.

Stage 3

The product from Stage 2 was dissolved in water (1.5l) by addition of concentrated NH_4OH to pH 9-9.5. This solution was added to 1N HCl (1000ml) and the product of Formula (A) (free acid) was filtered

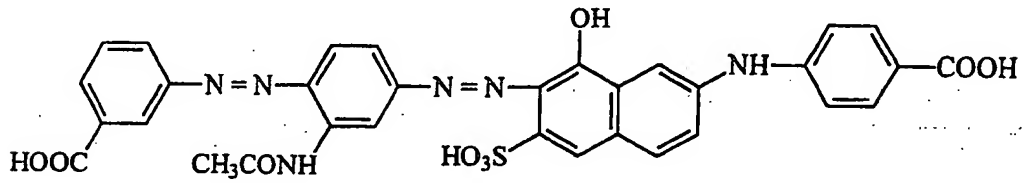
and washed with 1N HCl. The dissolution and re-precipitation procedure was repeated and the resultant paste was added to water (5l) and the pH adjusted to 9.0 with concentrated NH_4OH. The resulting solution was dialysed until Cl^- could no longer be detected, screened through a 0.45μm filter, and the product, the ammonium salt of the compound of Formula (A), isolated by evaporation.

Evaluation

The ammonium salt of the compound of Formula (A) (2.5 parts) was dissolved in a mixture of water (90 parts) and diethylene glycol (10 parts) and the solution printed onto plain paper using a thermal ink jet printer. The image had a strong, bluish-black shade with high water fastness. The compound also had good aqueous solubility.

Example 2

Preparation of the compound of Formula (B)



(B)

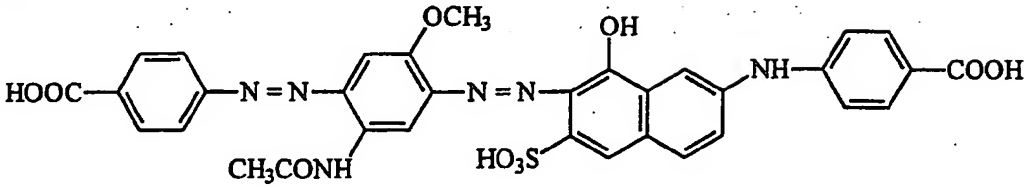
The procedure of Example 1 was repeated except that in place of the 3-amino-4-methoxyacetanilide used in Stage 1 there was used an equivalent amount of 3-aminoacetanilide.

Evaluation

When the ammonium salt of the compound of Formula (B) was made into an ink and applied to plain paper by ink jet printing by the method described in Example 1, the image had a strong black shade with high water fastness. The salt also had good aqueous solubility.

Example 3

Preparation of the compound of Formula (C)



(C)

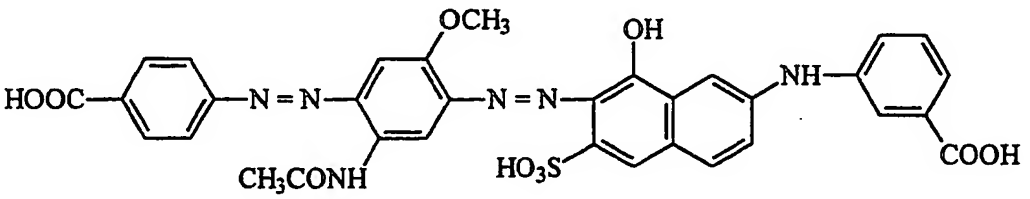
The procedure of Example 1 was repeated except that in place of the 3-aminobenzoic used in Stage 1 there was used the same amount of 4-aminobenzoic to produce the compound of Formula (C) as the ammonium salt.

Evaluation

When the ammonium salt of the compound of Formula (C) was made into an ink and applied to plain paper by ink jet printing by the method described in Example 1, the black image had similar properties to that of the image from the ink containing the compound of Formula (A).

Example 4

Preparation of the compound of Example (D)

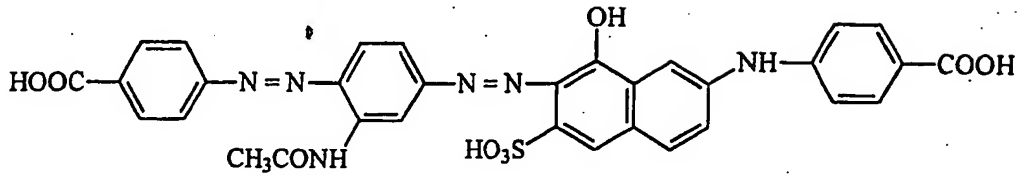


(D)

The procedure of Example 3 was repeated except that in place of the N-(4-carboxyphenyl)-Gamma acid used in Stage 2 there was used the equivalent amount of N-(3-carboxyphenyl)-Gamma acid to produce the ammonium salt of the compound of Formula (D).

Example 5

Preparation of the compound of Formula (E)

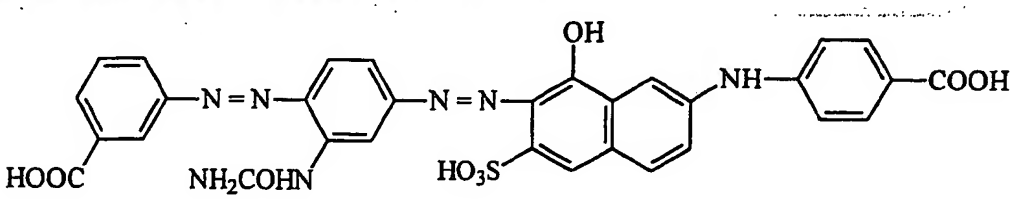


(E)

The procedure of Example 1 was repeated except that in place of the 3-aminobenzoic acid and 3-amino-4-methoxyacetanilide used in Stage 1 there was used the equivalent amounts of 4-aminobenzoic acid and 3-aminoacetanilide respectively to produce the ammonium salt of the compound of Formula (E).

Example 6

Preparation of the compound of Formula (F)



(F)

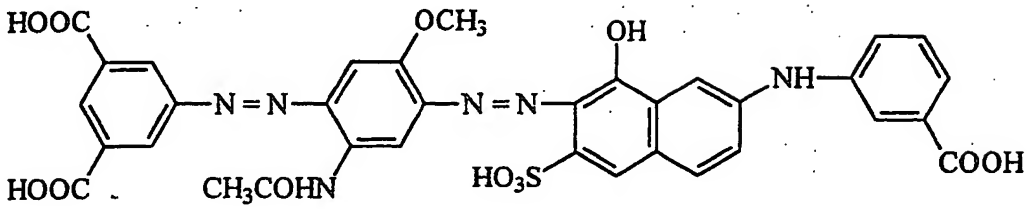
The procedure of Example 1 was repeated except that in place of the 3-amino-4-methoxyacetanilide used in Stage 1 there was used an equivalent amount of 3-ureidoaniline to produce the compound of Formula (F) as its ammonium salt.

Evaluation

When the compound of Formula (F) was made into an ink and applied to plain paper by ink jet printing by the method described in Example 1, the black image had similar properties to that of the image from the ink containing the compound of Formula (A) except that it was redder in shade.

Example 7

Preparation of the compound of Formula (G)

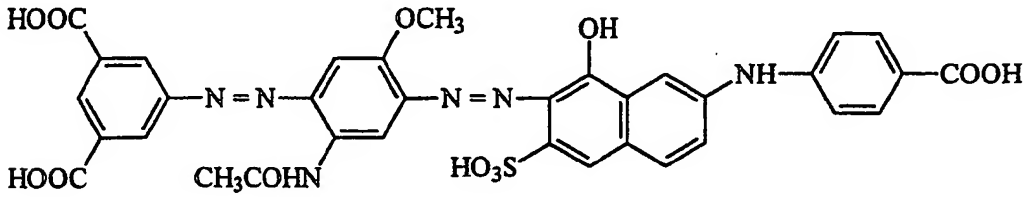


(G)

The method of Example 1 was repeated except that in place of the 3-aminobenzoic acid used in Stage 1 there was used an equivalent amount of 5-aminoisophthalic acid and in place of the N-(4-carboxyphenyl)-Gamma acid used in Stage 2 there was used the same amount of N-3-carboxyphenyl)-Gamma acid to product the compound of Formula G.

Example 8

Preparation of the Compound of Formula (H)



(H)

Stage 1

To a stirred suspension of aminoisophthalic acid (13.7g, 0.1M) in ice/water (150ml), 36°TW HCl (30ml) was added, followed by a solution of sodium nitrite (7g) in water (50ml), maintaining the temperature at 0-10°C by the addition of small quantities of ice as necessary. When the addition was complete the resultant diazo solution was stirred at
0-10°C for 1 hour and residual nitrous acid destroyed by the addition of sulphamic acid (10% solution).

3-amino-4-methoxyacetanilide (20g, 0.1M) was dissolved in methylated spirits 740P (500ml) and added to the above diazo solution. The mixture was stirred for 18 hours at 20-25°C. The precipitated product was filtered off and the filter cake washed with water (500ml).

Stage 2

The paste from Stage 1 was dissolved in water (500ml) at room temperature with the addition of 2N NaOH to give a complete solution at pH 9. Sodium nitrite solution (7g) in water (50ml) was added and the reaction mixture acidified by adding to a mixture of 36°Tw HCl (30ml) and ice-water (150ml) over 10 minutes, maintaining temperature at 0-10°C. After 2 hours at 0-10°C the excess nitrous acid was destroyed by addition of sulphamic acid to give a diazo solution.

A solution of Gamma acid was prepared by dissolving Gamma acid (26.5g, 0.1M) in water (400ml) with the addition of 2N NaOH to raise the pH to 9.0 followed by $NaCO_3$ (10g) and the solution cooled to 0-10°C.

The diazo solution was added slowly over 10 minutes to the Gamma acid solution, maintaining the pH at 9-10 by addition of 2N NaOH solution and then stirred for 1 hour at 0-10°C. The mixture was heated to 50-60°C and salted to 7% with NaCl. The precipitated product of Formula (H) (mainly as Na salt) was washed with 10% NaCl.

Stage 3

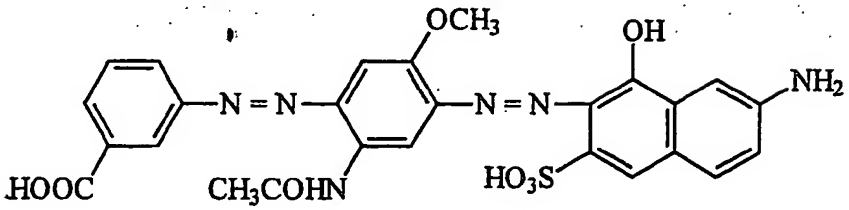
The paste from Stage 2 was dissolved in water (500ml) by the addition of NH_4OH to pH 9.5 and the solution slowly added to 1N 2HCl (1000ml). The compound, in free acid form, was filtered and washed with 1N HCl. The paste was added to water (500ml) and the pH adjusted to 9.0-9.5 with concentrated ammonium hydroxide solution. The solution was dialysed until chloride ion could no longer be detected, screened through a 0.45μm filter, and all water evaporated off to produce the compound of Formula (H) as ammonium salt.

Evaluation

When the ammonium salt of the compound of Formula (H) was made into an ink and applied to plain paper by ink jet printing by the method described in Example 1, the black image had similar properties to that of the image from the ink containing the compound of Formula (A).

Example 9

Preparation of the Compound of Formula (J)

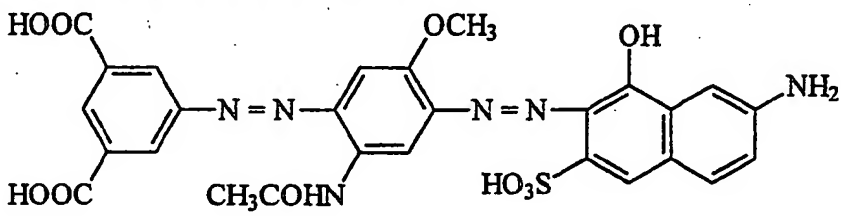


(J)

The method of Example 1 was repeated except that in place of the N-4-carboxyphenyl)-Gamma acid there was used the equivalent amount of Gamma acid to produce the compound of Formula (J) as ammonium salt.

Example 10

Preparation of the compound of Formula (K)

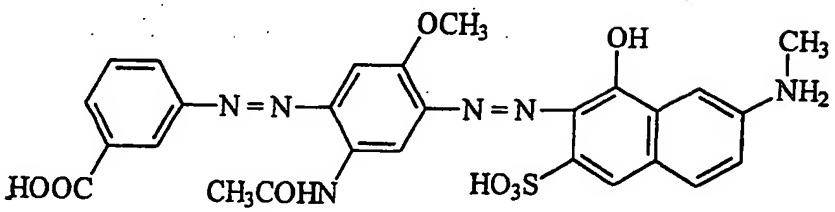


(K)

The method of Example 1 was repeated except that in place of the 3-aminobenzoic acid used in Stage 1 there was used 5-amino-isophthalic acid (18.1g) and in place of the N-4-carboxyphenyl)-Gamma acid there was used the equivalent amount of Gamma acid to produce the compound of Formula (K) as ammonium salt.

Example 11

Preparation of the compound of Formula L



(L)

The method of Example 1 was repeated except that in place of the N-(4-carboxyphenyl)-Gamma acid there was used the equivalent amount of N-methyl-Gamma acid to produce the compound of Formula (L) as ammonium salt.

Example 12

Further inks may be prepared having the compositions described in Tables 1 and 2 below wherein Inks 1-5 contain the compound of Formula (A), Inks 6-10 contain the compound of Formula (B), Inks 11-15 contain the compound of Formula (C), Inks 16-20 contain the compound of Formula (D), Inks 21-25 contain the compound of Formula (E), Inks 26-30 contain the compound of Formula (G) and Inks 30 to 34 the compound of Formula (H).

The following abbreviations are used in Tables 1 and 2:

PG	= propylene glycol	DEG	= diethylene glycol
NMP	= N-methyl pyrrolidone	DMK	= dimethylketone
IPA	= isopropanol	MEOH	= methanol
2P	= 2-pyrrolidone	MIBK	= methylisobutyl ketone
TDG	= thiodiglycol	BDL	= butane-2,3-diol
PHO	= Na_2HPO_4	DMA	= dimethylamine
CET	= cetyl ammonium bromide (surfactant)		

Table 1

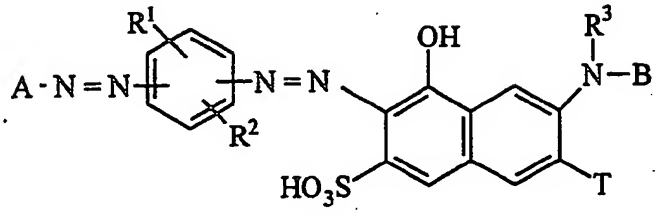
Ink No.	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	DMA	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2					
3	1.0	85	5		2	2		0.1		5	1	
4	2.1	91		8								1
5	3.1	86	5					0.2	4			5
6	1.1	81			9		0.5	0.5			9	
7	2.5	60	4	15	3	3			6	10	5	4
8	1.9	70		20					10			
9	2.4	75	5	4		5				6		5
10	4.1	80	3	5	2	10		0.3				
11	3.2	65		5	4	6			5	4	6	5
12	4.6	96								4		
13	0.8	90	5						5			
14	1.2	80	2	6	2	5			1		4	
15	1.8	80		5							15	
16	2.6	84			11						5	
17	3.3	80	2			10				2		6
18	1.7	90				7	0.3		3			
19	1.5	69	2	20	2	1					3	3
20	1.6	91			4						5	

Table 2

Ink No.	Dye Content	Water	PG	DEG	NMP	CET	TBT	Na Stearate	BDL	PHO	2P	TDG
21	3.0	80	15			0.2					5	
22	2.0	90		5						1.2		5
23	1.5	85	5	5		0.15	5.0	0.2				
24	2.5	90		6	4					0.12		
25	3.1	82	4	8		0.3						6
26	0.9	85		10					5	0.2		
27	1.5	90		5	5			0.3				
28	2.9	70		10	4				1		4	11
29	2.2	75	4	10	3				2		6	
30	2.6	91			6						3	
31	3.2	76		9	7		3.0			0.95	5	
32	4.0	78	5	11							6	
33	3.3	86			7						7	
34	1.1	70	5	5	5	0.1	0.2	0.1	5	0.1	5	5

Claims

1. A compound of the Formula (1) and salts thereof:



Formula (1)

wherein:

A is optionally substituted phenyl or naphthyl;
R^1 is NR^4R^5;
R^2 is H, halo, -COOH, $-SO_2OH$, optionally substituted alkyl, alkoxy or alkylthio;
R^3 & R^4 are each independently is H or optionally substituted alkyl;
R^5 is optionally substituted acyl;
T is H or sulpho; and
B is H, optionally substituted alkyl or phenyl.

provided that the compound does not contain a piperazinyl group.

2. A compound according to Claim 1 wherein A is selected from 3-carboxyphenyl, 4-carboxyphenyl, 3,5-dicarboxyphenyl and 3,4-dicarboxyphenyl.

3. A compound according to Claim 1 or Claim 2 wherein R^1 is $-NHCO-C_{1-4}$-alkyl.

4. A compound according to any one of Claims 1 to 3 wherein R^2 is selected from H, methyl, methoxy, chloro, $-SO_2OH$ and -COOH.

5. A compound according to any one of Claims 1 to 4 wherein B is selected from phenyl, 3-carboxyphenyl, 4-carboxyphenyl, 3,5-dicarboxyphenyl, H and methyl.

6. A compound selected from the group comprising
1-hydroxy-2-[2-methoxy-4-(3-carboxyphenylazo)-5-acetylamino-phenylazo]-3-sulpho-7-(4-carboxyphenylamino)-naphthalene;
1-hydroxy-2-[2-methoxy-4-(3-carboxyphenylazo)-5-ureido-phenylazo]-3-sulpho-7-(4-carboxyphenylamino)-naphthalene; and

1-hydroxy-2-[2-methoxy-4-(3,5-dicarboxyphenylazo)-5-acetylamino-phenylazo]-3-sulpho-7-(4-carboxyphenylamino)-naphthalene.

7. A compound according to any one of Claims 1 to 6 in the form of the ammonium or substituted ammonium salt.

8. An ink comprising a compound according to any one of Claims 1 to 7 and a liquid medium.

9. An ink according to Claim 8 wherein the liquid medium is water or a mixture comprising water and a water-soluble organic solvent.

10. A process for printing a substrate by ink jet printing using an ink according to Claim 8 or Claim 9.

The Patent Office

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Application No:	GB 9509935.4	**Examiner:**	Dr. A.J.Rudge
Claims searched:	1-10	**Date of search:**	10 August 1995

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): C4P(PAZ)

Int Cl (Ed.6): C09B-031/08

Other: ONLINE DATABASES: CAS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	None	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.